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COLLECTING METHOD FOR THERMOPLASTIC RESIN  
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Specification

1. Title of the Invention

Collecting Method for Thermoplastic Resin

2. What is Claimed is:

1. A collecting method for thermoplastic resin which collects thermoplastic resin from thermoplastic resin emulsion, characterized in that the addition of coagulating agents is carried out in two or more processes: in the first process, a coagulating agent and/or a coagulating aid is added and, in the second process, a coagulating agent or a coagulating agent and a coagulating aid are added, with the solution temperature being higher than that of the first temperature.

2. The collecting method for thermoplastic resin in accordance with Claim 1, characterized in that, in the first process, the solution after a coagulating agent and/or a coagulating aid have been added has a pH of 3 to 7.

3. The collecting method for thermoplastic resin in accordance with Claim 1, characterized in that, in the solution after a coagulating agent and/or a coagulating aid have been added in the first process, greater than 50% of

the resin emulsion is coagulated and the coagulation has not been completed.

### 3. Detailed Description of the Invention

The present invention relates to collecting methods for a thermoplastic resin and, more specifically, to a collecting method for a thermoplastic resin where the thermoplastic resin is collected by adding a coagulating agent to a thermoplastic resin emulsion.

Previously, when a resin is collected from a thermoplastic resin emulsion manufactured by an emulsion polymerization method, a coagulating agent, such as hydrochloric acid, is generally used to coagulate the emulsion. The process can be conducted, for example, by introducing a thermoplastic resin emulsion into an aqueous solution in which a coagulating agent has been dissolved, coagulating the resin constituent and collecting it, or by introducing a solution in which a coagulating agent has been dissolved into a thermoplastic resin emulsion, coagulating the resin and collecting it.

However, the resin powder collected by the conventional coagulating method has varied particle size and contains a substantial amount of fine particles and coarse particles, and the shape of the particles is not uniform; therefore, the following problems may be posed:

(1) When the powder contains a large amount of fine particles, the fine-particle powder may flow out or splash during separating/collecting resin from thermoplastic resin latex and drying the resin; therefore, the work environment may become impaired due to the loss of resin and the generation of dust and a dust explosion may be caused.

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(2) The fine particles and coarse particles in the powder may cause clogging in the apparatuses during the separating and drying processes; therefore, the productivity may become impaired and a large amount of energy may be wasted.

(3) With the non-uniform shape of the particles, when the powder is stored in a hopper, a bag or the like, the powder may cause blocking, preventing the powder from readily removed; therefore, the handling properties may become significantly impaired.

The above-described problems (1) to (3) can be solved by the improvement of equipment, but improvements are limited and require considerable expense.

The present invention intends to solve the problems of conventional techniques and provide a collecting method for thermoplastic resin where a powder having a particle-size distribution that is as small as possible and a particle shape being approximately spherical can be obtained.

In order to achieve the above-described objectives, the present inventors conducted intensive research and discovered that a resin powder having a particle shape being approximately spherical and a content of fine or coarse particles that is small could be obtained by coagulating a thermoplastic resin latex in two or more processes. The present invention is based on this discovery.

More specifically, the present invention is a collecting method for thermoplastic resin which collects thermoplastic resin from thermoplastic resin emulsion, characterized in that the addition of coagulating agents is carried out in two or more processes: in the first process, a coagulating agent and/or a coagulating aid is added and, in the second process, a coagulating agent or a coagulating agent and a coagulating aid are added, with the solution temperature being higher than that of the first temperature.

The above-described two or more processes in the present invention can be generally conducted using a coagulation tank twice or more but is not restricted to the method; for examples, a cylindrical vessel having two or more compartments and equipped with a stirrer for each compartment can be used. Further, a so-called "batch method" can be applied, wherein the second process is

immediately initiated once the first process has been completed in the same coagulating tank.

Commonly-known thermoplastic resin emulsions can be used in the present invention. Known examples of the thermoplastic resins include graft copolymers that can be obtained by polymerizing one or more monomers, such as unsaturated nitrile monomers, aromatic vinyl monomers, (meth)acrylic acid ester monomer or monomers that can be co-polymerized with the above-described monomers in the presence of conjugated diene rubbers, conjugated diene copolymers (e.g., polybutadiene, butadiene-styrene copolymer and butadiene-acrylonitrile copolymer) or ethylene-propylene copolymers. Known specific examples of the graft copolymers include ABS resin, ethylene-propylene rubber-modified styrene-acrylonitrile resin, methyl methacrylate/butadiene-styrene resin (MBS resin) and high-impact polystyrene resin (HIPS resin). In particular, the resin having a rubber content of greater than 45 wt% can effectively improve the anti-blocking properties. The inventive method is particularly effective in improving the powder properties of rubber-modified thermoplastic resins but can also be applied to thermoplastic resin emulsions, such as ethylene vinyl acetate copolymer (EVA), vinyl

chloride copolymer, styrene-acrylonitrile copolymer, styrene polymer, and high styrene-butadiene copolymer.

In the inventive method, typically, two or more coagulating tanks are prepared, a coagulating agent and/or a coagulating aid are introduced into the first coagulating tank, and a coagulating agent or a coagulating agent and a coagulating aid are introduced into the second coagulating tank, yielding the desired resin powder.

Known examples of the coagulating agents that can be used in the present invention include inorganic acids, such as hydrochloric acid and sulfuric acid, inorganic salts, such as calcium chloride and magnesium sulfate, organic acids, such as formic acid and acetic acid, and organic salts, such as aluminum acetate. Of these, inorganic acids are particularly preferred.

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Known examples of the coagulating aids that can be used in the present invention include water-soluble high molecular compounds, such as polyethylene oxide, polyvinyl alcohol, amines, imides, and amides. One or more of these coagulating agents and coagulating aids can be used in the first coagulating tank, the second and following coagulating tanks. The proportion of the coagulating agent and the coagulating aid varies depending on the type of the



thermoplastic resin latex, but can be appropriately determined according to the pH value of the slurry in the coagulating tank, the coagulation state of the slurry and the particle state of the powder. If the proportion of the coagulating agent and the coagulating aid is too high, the water washability may become impaired, prolonging the washing time and requiring a large amount of water; thus, it is not economically advantageous. If the proportion is too low, the thermoplastic resin emulsion may not be completely coagulated, resulting in noncondensables remaining in the slurry; therefore, the collection rate of the resin may become low and operations in the separating/drying processes may be disrupted.

A coagulating agent and a coagulating aid used in the present invention can be appropriately selected according to the type of soaps contained in the thermoplastic resin emulsion. General coagulating agents and coagulating aids can sufficiently coagulate resin acid soaps, fatty acid soaps and the like, but coagulating agents and coagulating aids consisting essentially of organic salts, inorganic salts and water-soluble high molecular compounds can be preferably used to coagulate phosphate ester soaps, sulfate ester soaps, sulfonic acid ester soaps and cationic soaps.

Any coagulating tanks can be used in the processes of the present invention as long as an appropriate stirrer is equipped. Known examples of the coagulation tanks include general stirrers, such as propeller blades and flat blades, and stirrers, such as spiral agitators and homogenizers having a high shearing force. A thermoplastic resin emulsion, a coagulating agent and a coagulating aid can be separately introduced into the first coagulating tank, or can also be mixed in advance in a mixing vessel or a line mixer and the mixture can be introduced into the first coagulating tank.

The slurry in the first coagulating tank is preferably in an partially coagulated state where the stability of the emulsion is partially destroyed and the coagulation has not been completed, and, in order to achieve such a state, the pH of the slurry is preferably 3 to 7, more preferably 3 to 6. In the partially coagulated state, greater than 50% of an emulsion has been coagulated and the coagulation has not been completed. When the slurry is filtered using a Toyo filter paper No. 131 (the third type described in JIS P3801), greater than 50% of the polymer preferably remains on the filter paper and the filtrate is preferably opaque. The slurry temperature in the first coagulation tank is lower than that of the second and following coagulation

tanks and is preferably lower by 10 degrees Celsius. The pH of the slurry in the first coagulating tank is less than 3, the shape of the resulting resin powder particles may not become uniform, whereas if the pH is greater than 7, a content of the fine particles in the resulting resin powder may become large. Further, if the slurry temperature in the first coagulating tank becomes higher than the slurry temperature in the second coagulating tank, the resulting powder may have a large particle-size distribution.

The coagulation of the slurry must be completed in the second or following processes; therefore, when a coagulating agent used consists essentially of acidic coagulating agents, such as organic acids and inorganic acids, the pH of the slurry in the second or following processes is preferably 1 to 3, and when a coagulating agent used consists essentially of inorganic salts and organic salts, and a coagulating aid is additionally used, the proportion thereof is preferably determined by observing the coagulation so that the pH of the slurry is in a range of 2 to 7.

The slurry temperature in the coagulating tank is generally 0 to 100 degrees Celsius, preferably room temperature to 100 degrees Celsius. The slurry temperature in the second and following processes varies depending on

the type of the thermoplastic resin emulsion and can be therefore determined while observing the properties of the powder and the coagulating status. If the slurry temperature is too high, the particles may coagulate excessively, generating coarse particles, whereas the slurry temperature is too low, the resulting powder particles may become fine particles before the coagulation is completed.

As described above, thanks to the present invention, thermoplastic resin powder having a uniform particle size can be continuously and efficiently collected. Since the resulting resin powder has approximately spherical particles, a small particle-size distribution and a small repose angle, blocking can be prevented and a powder that can be readily handled in the industrial production can be obtained.

The embodiments of the present invention are explained. The terms "part" and "%" should be construed as "part by weight" and "wt%". The anti-blocking properties, particle-size distribution, repose angle and particle shape were measured by the following methods.

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(1) Evaluation of anti-blocking properties

3 mg of resin powder was introduced into a cylindrical metal mold having a diameter of 4 cm and was loaded at room temperature for 15 seconds in order to measure the minimum load G (kg) which the resin mold could obtain.

Anti-blocking properties ( $\text{kg}/\text{cm}^2$ ) =  $G \text{ (kg)} / \text{cross-section area of mold (cm}^2\text{)}$

A larger value prevents more blocking.

## (2) Measuring method of particle-size distribution

Conditions are as follows:

Shaker: ro-tap shaker

Shaking time: 20 minutes

Sieve: standard sieve (JIS 28801)

Sample: 50 mg

The residue A (%) on the sieve is obtained.

$\text{Residue (\%)} = (A/\text{all sample}) \times 100$

A: residue on the sieve after shaking.

According to the results of the test, the particle size distribution of the powder can be revealed.

## (3) Measuring method of repose angle

The repose angle was measured by a repose angle meter AN-1, manufactured by Showa Engineering Co., Ltd., according to the measuring method of AN-1. The disintegration rate increases as the repose angle becomes smaller and the powder bridge can be prevented when the

powder is removed from a hopper; thus, the powder can be readily removed while preventing blocking.

#### (4) Microscopic observation

The shape of the particles of the resin constituent in the slurry after coagulation and the shape of the particles in the powder were observed using a light microscope, with the magnification being  $\times 200$ .

#### Embodiment 1

MBS resin emulsion having a solid content concentration of 30% was prepared as a thermoplastic resin emulsion by graft-polymerizing 35 parts styrene and 20 parts methyl methacrylate with 45 parts styrene-butadiene rubber copolymer. The resulting MBS resin emulsion and sulfuric acid were introduced from separate pumps into a first coagulating tank equipped with a stirrer, yielding a slurry having a pH of 4.0. The amount of the sulfuric acid supplied was adjusted so that the resulting slurry had a pH of 4.0. The slurry was introduced into a second coagulating tank and sulfuric acid was continuously introduced into the second coagulating tank so that the slurry had a pH of 2.5. The temperature of the coagulating tanks was the free air temperature in the first coagulating tank and 85 degrees Celsius in the second coagulating tank. Resin constituent was separated from the slurry in the second coagulating

tank by using a centrifugal separator, washed with water, and dried, yielding a resin powder.

#### Comparative Example 1

A resin powder was obtained by the same method as Embodiment 1, except that the total amount of sulfuric acid supplied in Embodiment 1 was continuously introduced into the first coagulating tank in order to adjust the pH to 2.5 and no sulfuric acid was introduced into the second coagulating tank (by a conventional method).

The particle-size distribution, repose angle and anti-blocking properties of the resin powders obtained in Embodiment 1 and Comparative Example 1 were shown in Table 1. Microphotographs ( $\times 200$ ) of the particle shape of the resin dry powder are shown in Fig. 1 and Fig. 2. Fig. 1 is Embodiment 1 and Fig. 2 is Comparative Example 1.

[Table 1]

	Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4
Coagulating agent in the first coagulating tank	Sulfuric acid	Sulfuric acid	Sulfuric acid	Sulfuric acid Polyethylene oxide
Slurry pH of the coagulating agent in the first coagulating tank	4.0	3.0	7.0	6.0
Coagulating agent in the second coagulating tank	Sulfuric acid	Sulfuric acid	Sulfuric acid	Sulfuric acid
Slurry pH of the coagulating agent in the second coagulating tank	2.5	2.5	2.5	2.5
Particle-size distribution				
20 mesh ON (%)	0.7	4.8	2.0	1.2
28 mesh ON (%)	1.2	4.5	1.8	1.5
35 mesh ON (%)	4.0	6.9	2.2	4.1
48 mesh ON (%)	13.3	12.8	14.6	14.9
70 mesh ON (%)	27.2	23.8	20.4	26.9
100 mesh ON (%)	36.0	37.8	34.0	42.3
150 mesh ON (%)	11.1	5.5	8.4	6.2
200 mesh ON (%)	5.1	2.1	6.7	1.7
200 mesh PASS	1.4	1.8	9.9	1.2
Repose angle	35	38	39	34
Anti-blocking properties (kg/cm <sup>2</sup> )	0.52	0.45	0.43	0.58



[Table 1] (Cont'd)

	Embodiment 4	Embodiment 5	Comparative Example 1	Comparative Example 2
Coagulating agent in the first coagulating tank	Polyethylene oxide	Sulfuric acid	Sulfuric acid	Sulfuric acid
Slurry pH of the coagulating agent in the first coagulating tank	7.0	4.0	2.5	2.5
Coagulating agent in the second coagulating tank	Sulfuric acid	Sulfuric acid	-	-
Slurry pH of the coagulating agent in the second coagulating tank	2.5	2.5	2.5	2.5
Particle-size distribution				
20 mesh ON (%)	1.9	2.3	11.4	9.3
28 mesh ON (%)	2.1	2.8	8.4	7.5
35 mesh ON (%)	2.1	9.6	7.9	6.4
48 mesh ON (%)	17.1	18.2	8.0	9.2
70 mesh ON (%)	23.2	32.5	8.8	14.9
100 mesh ON (%)	46.2	26.7	10.7	18.1
150 mesh ON (%)	4.8	2.7	7.1	8.5
200 mesh ON (%)	1.4	3.2	14.5	9.8
200 mesh PASS	1.2	2.0	23.2	16.3
Repose angle	34	32	44	43
Anti-blocking properties (kg/cm <sup>2</sup> )	0.58	0.68	0.26	0.35

As is clear from the results shown in Table 1, as for the particle-size distribution, the powder obtained in Embodiment 1 had a smaller content of coarse particles and fine particles than the powder obtained by a conventional method in Comparative Example 1; therefore, the powder obtained in Embodiment 1 was found to have uniform particles. Further, the powder obtained in Embodiment 1 had a smaller repose angle than Comparative Example 1, indicating a high flowness, and had a high anti-blocking properties, preventing blocking. According to the microphotographs, the particles of the powder in Comparative Example 1 (Fig. 2) are non-uniform while the particles of the powder in Embodiment 1 (Fig.1) are spherical.

#### Embodiment 2

A resin powder was obtained by the same method as Embodiment 1, except that the amount of sulfuric acid supplied was adjusted so that the pH of the slurry in the first coagulating tank became 3.0. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder were shown in Table 1.

#### Embodiment 3

A resin powder was obtained by the same method as Embodiment 1, except that the amount of sulfuric acid supplied was adjusted so that the pH of the slurry in the

first coagulating tank became 7.0. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder were shown in Table 1.

#### Embodiment 4

Examples of the combination of coagulating aids are explained in the following. A resin powder was obtained by the same method as Embodiment 1, except that sulfuric acid and 7.5% the weight of sulfuric acid of polyethylene oxide (molecular weight:  $430 \times 480 \times 10^4$ ) were introduced into the first coagulating tank so that the pH of the slurry in the first coagulating tank became 6.0. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder were shown in Table 1.

#### Embodiment 5

A resin powder was obtained by the same method as Embodiment 1, except that 0.09 parts by weight of the polyethylene oxide in Embodiment 4 as against 100 parts by weight of the resin constituent in the slurry were introduced in the first coagulating tank as a coagulating aid so that the pH of the slurry in the first coagulating tank became 7.0. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder were shown in Table 1.

#### Embodiment 6

A resin powder was obtained by the same method as Embodiment 1, except that a thermoplastic resin emulsion having a solid content concentration of 45% styrene, 17% acrylonitrile and 38% butadiene by graft-polymerizing a mixture of polybutadiene, styrene and acrylonitrile was used. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder were shown in Table 1.

#### Comparative Example 2

A resin powder was obtained by the same method as Embodiment 1, except that the thermoplastic resin emulsion used in Embodiment 6 was continuously introduced into the first coagulating tank from a pump, the total amount of the sulfuric acid introduced into the first coagulating tank 1 and the second coagulating tank 2 in Embodiment 6 was introduced into the first coagulating tank 1 and no sulfuric acid was introduced into the second coagulating tank. The pH of the first coagulating tank was adjusted to 2.5. The particle-size distribution, repose angle and anti-blocking properties of the resulting resin powder obtained in the second coagulating tank were shown in Table 1

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#### 4. Brief Description of the Drawings

Fig. 1 and Fig. 2 are microphotographs ( $\times 200$ ) of the cross-section of the powder obtained in the second coagulating tank in Embodiment 1 and Embodiment 2.

Agent: Takenaga Kawakita, Patent Attorney

Fig. 1

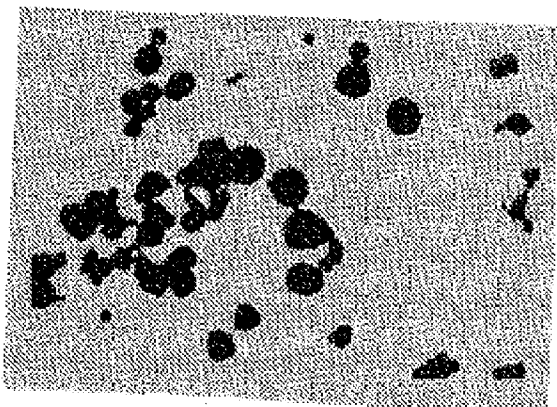


Fig. 2



Amendment of Proceedings (System)

3/7/1983

Commissioner: Kazuo Wakazugi

1. Identification of Case

Japanese Patent No. 200359 (1982)

2. Title of the Invention

Collecting Method for Thermoplastic Resin

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6. Items Amended: Application and Specification

7. Contents Amended: The details are given on the attached sheet. (No modification in the Application and Emgrossment of Specification and its content)